JOC The Journal of Organic Chemistry
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# Catalyst-Free Rearrangement of Allenyl Aryldiazoacetates into 1,5-Dihydro-4*H*-pyrazol-4-ones

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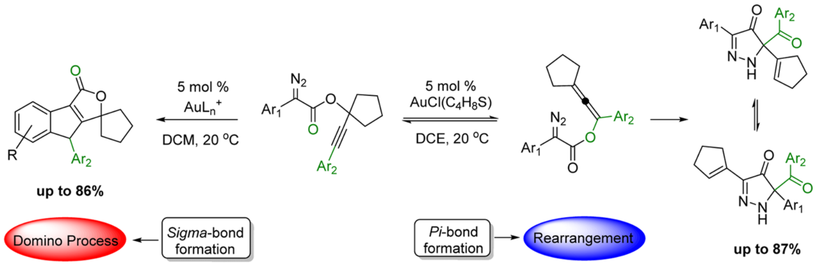
S *Supporting Information*



**ABSTRACT:** Phenylpropargyl diazoacetates exist in equilibrium with 1-phenyl-1,2-dien-1-yl diazoacetate - allenes that are rapidly formed at room temperature through 1,3-acyloxy migration catalyzed by gold(I) or gold(III) compounds, and these catalysts react solely with the π-donor rather than with the diazo group. The product allene of the aryldiazoacetates undergoes rearrangement that is not catalyzed by gold in which the terminal nitrogen of the diazo functional group adds to the central carbon of the allene, initiating a sequence of bond-forming reactions, resulting in the production of 1,5-dihydro-4*H*-pyrazol-4-ones in good yields. These 1,5-dihydro-4*H*-pyrazol-4-ones undergo intramolecular 1,3-acyl migration to form an equilibrium mixture and can quantitatively transfer the acyl group to an external nucleophile with formation of 4-hydroxypyrazoles. Reactions of phenylpropargyl phenyldiazoacetates catalyzed by cationic gold complexes are initiated at the diazo functional group to form a gold carbene whose subsequent cascade process (intramolecular addition, then aromatic substitution) results in the formation of a product that is uniquely characteristic of this pathway.

## INTRODUCTION

Gold catalysis provides powerful methodologies for unique metallo-organic transformations.[1] Activation of organic functional groups by gold(I) and gold(III) complexes initiates diverse pathways for often unique reactions.[2] One of the most useful of these transformations has been that of propargyl esters,[3] which form allenes by 1,3-acyloxy migration, that undergo varied catalytic reactions and in the presence of weak bases are converted to conjugated dienes.[4] We have been intrigued with the reactions of propargyl diazoacetates because these substrates contain two reactive centers for gold catalysts, and both are known to initiate reaction processes that are characteristic of their requisite functional groups.[2,5] In particular, the diazo functionality of a propargyl phenyldiazoacetate is expected to react with the gold catalyst that functions as a metallo-σ-bond acceptor to displace dinitrogen through back-donation and form a metal carbene. This metal carbene is proposed to undergo intramolecular addition to the proximal carbon−carbon triple bond to form a derivative metal carbene that completes the domino transformation by electrophilic substitution into the aromatic nucleus of the original aryldiazoacetate (Scheme 1).[6,7] π-Bond-forming reactions by gold catalysts that occur initially at the carbon−carbon triple bond proceed by nucleophilic addition, then 1,3-acyloxy migration, to a gold-coordinated allene[8] from which an acylium ion intermediate[9] may be the key to undetermined product(s). Both pathways are well-documented, although the product outcome of the π-bond initiated pathway is revealed here for the first time.

## RESULTS AND DISCUSSION

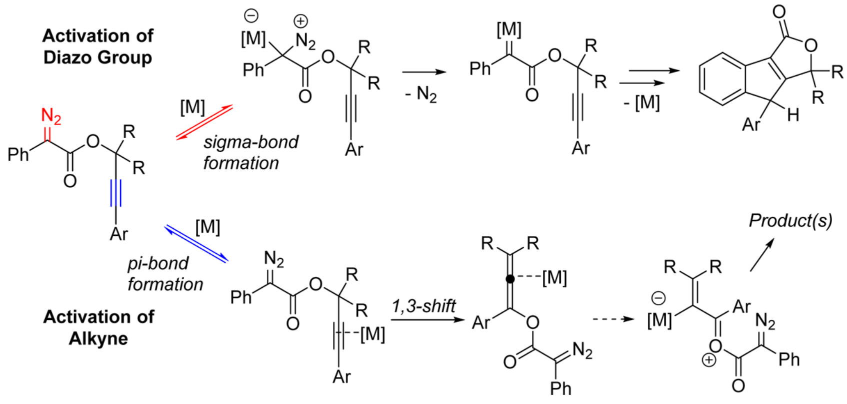
**Selectivity.** Initial assessment of gold catalysis was evaluated with propargyl aryldiazoacetates using cationic gold(I) catalysts, including those formed from ligated gold(I) chloride and silver salts. Cationic gold catalysts are well-established σ-bond acceptors with aryldiazoacetates,[5] and they have been widely used for dinitrogen extrusion reactions of diazo compounds that are reported to produce the corresponding gold carbenes. Catalytic reactions of phenylpropargyl phenyldiazoacetate **1** with representative $Au(I)^+$ catalysts formed the product from the carbene-initiated domino transformation **2** in good yield (Scheme 2). Complete conversion of the reactant was observed at room temperature, and no other discernible product was identified. Each of the gold catalysts was soluble in the reaction solution.

Neutral gold(I) and gold(III) compounds are reported to have varying influences on reactions with diazo and alkyne functional groups.[1,2,5] A survey of representative compounds

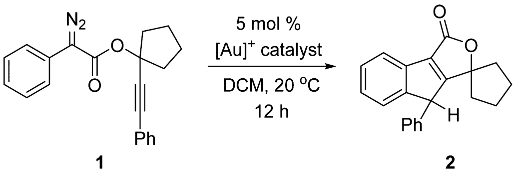
**Received:** July 28, 2016
**Published:** September 8, 2016

DOI: 10.1021/acs.joc.6b01833
*J. Org. Chem.* 2016, 81, 9235−9246

Scheme 1. Catalyst-Dependent Divergence of Reaction Pathway Based on σ-Bond Association with a Diazo Functional Group versus π-Bond Association with an Alkyne



Scheme 2. Domino Reaction of Propargyl Phenyldiazoacetate 1 Catalyzed by Cationic Gold(I)



| | |
|---|---|
| [Au(JohnPhos)(MeCN)]SbF$_6$ | 86% |
| AuCl(PPh$_3$)/AgSbF$_6$ | 83% |
| (IPr)AuCl/AgSbF$_6$ | 67% |

for reactions with **1** at 20 °C revealed that 5 mol % of chloro(tetrahydrothiophene)gold(I) [AuCl($C_4H_8S$)] catalyzed its complete conversion to three discernible products in the highest yield (Scheme 3). The surprising conversion of **1** to **3** and **4** retained all of the atoms of the reactant but gave extensive rearrangement, including the conversion of the reactant ester to product 1,5-dihydro-4*H*-pyrazol-4-ones.

Compounds **3** and **4** were observed spectroscopically to be related as structural isomers, and the crystal structure of **4** was obtained (Figure 1a) after its isolation from the reaction mixture. Recognition of **3** and **4** as potential benzoyl transfer agents prompted us to convert **3** and **4**, individually and as a mixture, quantitatively to the same 4-hydroxypyrazole **6** by treatment with nucleophilic bases that included hydrazines and amines (X-ray structure of analogue **6′**, Figure 1b). Compound **5**, although present in very low yield, was confirmed by spectral and chromatographic comparison with the previously characterized compound.[10]

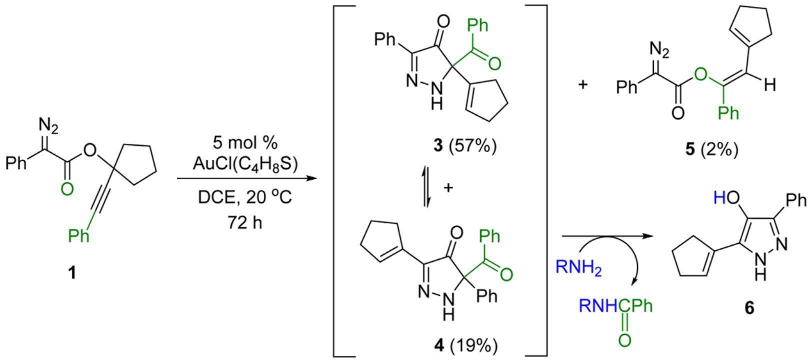
Examination of this reaction as a function of solvent did not provide any improvement in the product yield, but did show significant variation in the **3**:**4** product ratios (see the Supporting Information). To determine if this product variation could be due to an equilibrium between **3** and **4** under the reaction conditions, the formation of **3** and **4** in DCE was followed as a function of time over 10 days at room temperature with high product accountability, and the results from this investigation (Figure 2) clearly show an equilibrium between **3** and **4**.

Slow deacylation resulting in **6** complicates the overall picture, but conclusions can be drawn that compound **3** is the product of kinetic control at room temperature, and **4** is the product of thermodynamic control.

Experiments performed at higher temperatures (50 and 84 °C) are consistent with this interpretation. Compound **4** is the major isomer even at lower conversions of diazo compound **1**. At 50 °C, the maximum total yield of **3** + **4** is 81% at a 12 h reaction time, and the ratio **3**:**4** is 2:3, whereas, at 84 °C, the reaction is complete (total yield of **3** + **4** is 80%) after 6 h, and **3**:**4** is 1:1. Continuing the reaction further at these higher temperatures leads to lower product yield as the result of deacylation, from which 4-hydroxypyrazole **6** is formed.

Cationic gold(I) and the neutral chloro(tetrahydrothiophene)gold(I) catalysts are mutually exclusive for product formation from reactions with **1**. Both catalysts are active at room temperature, and their application provides products from reactions at the diazo functional group [**2** from cationic gold(I)] and the alkyne functional group [**3**, **4**, and **5** from AuCl($C_4H_8S$)] in good yields. Neutral gold(I) chloride

Scheme 3. Products from Gold(I)-Catalyzed Rearrangement of Phenylpropargyl Phenyldiazoacetate 1



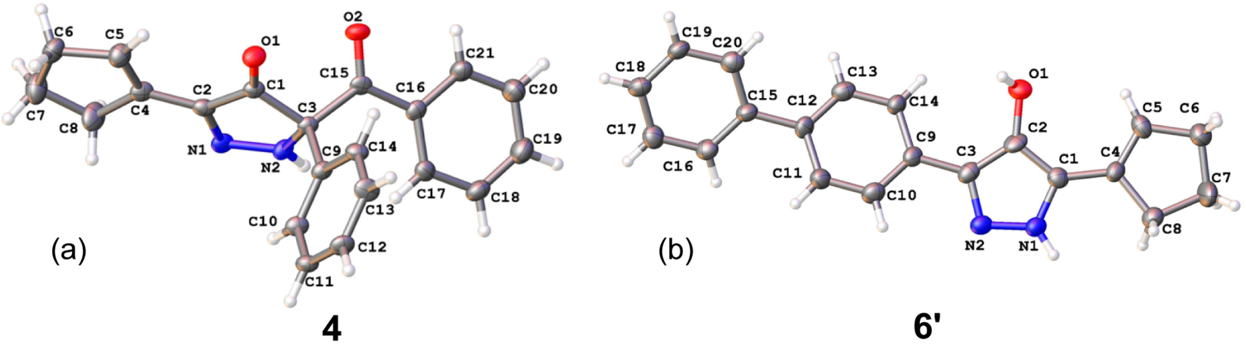


**Figure 1.** X-ray structures of 1,5-dihydro-4*H*-pyrazol-4-one **4** and deacylation product **6′** with 50% thermal ellipsoid probability.

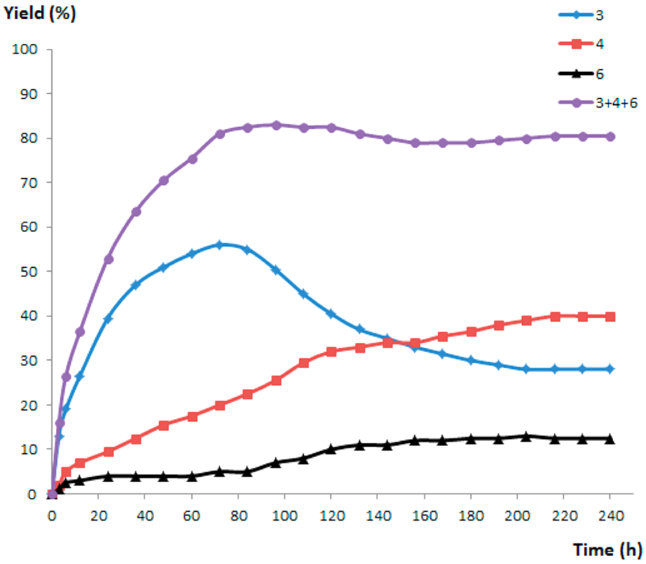
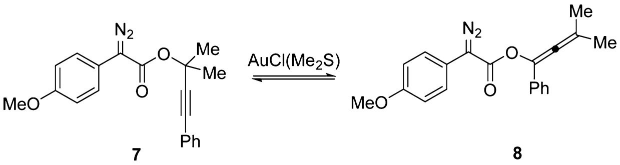


**Figure 2.** Time course for the formation of **3**, **4**, and **6** in DCE at 20 °C. Yields were determined by $^1$H NMR and HPLC analyses of the reaction mixture after selected periods of time using 1,3,5-trimethoxybenzene as the internal standard; reported yields are the averages of two runs.

complexes having strongly coordinating ligands (Table 1) show very low or negligible conversion of phenylpropargyl phenyldiazoacetate **1** under the same conditions, even to reaction times of 3 days.

However, heating these complexes to the temperature of refluxing 1,2-dichloroethane for up to 48 h gives **2** exclusively or as the major product (entries 1−6), albeit usually with low product yield and, generally, low % conversion.[11] The dimethylsulfide coordinated AuCl (entries 9 and 10) is not as effective a catalyst as its tetrahydrothiophene analogue (entries 7 and 8) with product yields only about half those found with AuCl($C_4H_8S$). Gold(III) catalysts (entries 11−14) are also less efficient than the AuCl($R_2S$) catalysts in the formation of compounds **3** and **4**. However, diene **5** is formed in the presence of these catalysts in yields up to 39%, and there is no evidence for the formation of **2**. In separate experiments, we have established that the dimethylsulfide ligand of AuCl remains on Au(I) throughout the reaction. Also, analysis by $^1$H NMR spectroscopy shows no apparent association of AuCl($Me_2S$) with the diazo functional group of methyl phenyldiazoacetate at room temperature, and <5% diazo decomposition occurred over 24 h.

**Role of Allene.** Close examination of the reaction process by NMR spectroscopy revealed that the key transformation in the formation of **3** and **4** was the generation of allene (Scheme 1), which occurred within 5 min at 20 °C. For these investigations, the dimethyl analogue (**7**) of cyclopentylpropargyl phenyldiazoacetate **1** was used (eq 1) to assess the course of the reaction. Allene **8** formation, which occurs by 1,3-acyloxy transfer, begins to take place immediately upon addition of the catalyst [5 mol % AuCl($Me_2S$) or AuCl($C_4H_8S$)] as the only reaction product, and reaches an apparent equilibrium (**7**:**8** = 45:55 with either catalyst).

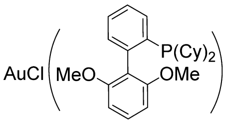


(1)

With added gold catalyst up to 2 equiv based on **7**, no further change in the **7**:**8** ratio occurred. Confirmation of this process was made with phenyldimethylpropargyl benzoate under the same conditions (allene:alkyne = 3:2) and with **1** (allene:alkyne = 1:2). The validity of the reversibility of Au(I)-catalyzed [3,3]-rearrangements of propargylic esters has been reported,[12] and with propargyl diazoacetates, additional stabilization by the diazo group of the cyclic carbocation intermediate on the pathway to allene formation could be expected. Furthermore, when the allene was isolated from the reaction mixture free of gold catalyst, the allene was observed to undergo slow conversion to the rearranged products corresponding to **3** and **4**, but without any obvious formation of **5**. This conversion was first-order in **7** with a rate constant of $1.05 \times 10^{-5}$ $s^{-1}$ at 20 °C, and addition of AuCl($Me_2S$) did not influence the reaction rate. The activation energy measured over 20−60 °C was 18.8 kcal/mol ($R^2 = 0.999$) with $\Delta H^\ddagger = 18.2$ kcal/mol and $\Delta S^\ddagger = -19.4$ cal/deg·mol at 298 K.

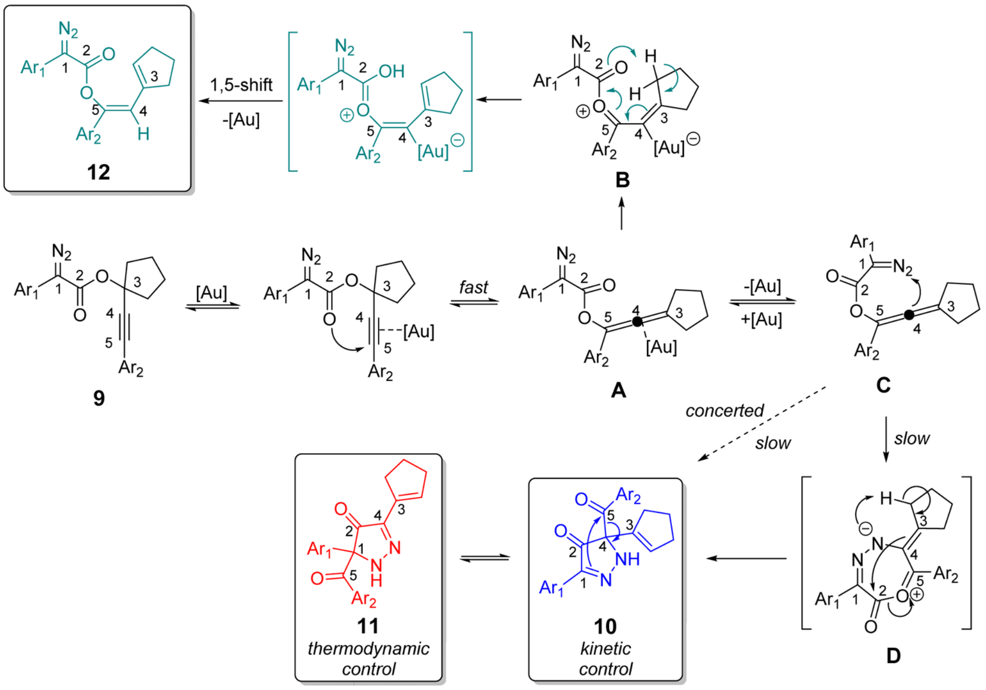
**Reaction Mechanism.** A stepwise mechanism for the neutral gold(I)-catalyzed rearrangement of arylpropargyl aryldiazoacetate **9** is given in Scheme 4. Consistent with the reported allene formation in related propargyl systems,[13] the AuCl($R_2S$)-catalyzed 1,3-acyloxy rearrangement of **9** produces carboxyallene **C** that undergoes a unique rearrangement between allene **C** and the diazo functional group to form the observed **3** directly in a concerted fashion or stepwise through intermediate **D**. The rearrangement of **C** to **10** is a rare example of a diazo compound reacting as an *N*-electrophile,[14] and the only one that involves an allene. Diene **12** is formed from gold-activated carboxyallene **A**, presumably through gold-coordinated acylium ion intermediate **B**. Compound **10** is formed

Table 1. Screening of Gold(I) and Gold(III) Catalysts in Reactions with Phenylpropargyl Phenyldiazoacetate **1**

| Entry[a] | Gold Catalyst | Temp (°C) | Conversion (%) **1** | Yield (%) **2**[b] | Yield (%) **3**+**4**[b] | Ratio **3**:**4**[b] | Yield (%) **5**[b] |
|---|---|---|---|---|---|---|---|
| 1 | AuCl(IPr) | 84[d] (20) | 68 (<5) | 46 | – | – | – |
| 2 | AuCl(CO) | 84 (20) | >95 (14) | 16 (9) | 14 | 47:53 | 9 |
| 3 | AuCl[P(OMe)$_3$] | 84[c] (20) | 40 (<5) | 25 | – | – | 3 |
| 4 | AuCl(PPh$_3$) | 84[c] (20) | 35 (<5) | 23 | – | – | – |
| 5 | AuCl(PMe$_3$) | 84[c] (20) | 45 (<5) | 20 | 8 | 40:60 | 6 |
| 6 |  | 84[c] (20) | 70 (<5) | 57 | – | – | – |
| 7 | AuCl(C$_4$H$_8$S)[i] | 20 | >95 | – | 76 | 75:25 | 2 |
| 8 | AuCl(C$_4$H$_8$S) | 84 | >95 | – | 80 | 45:55 | 4 |
| 9 | AuCl(Me$_2$S) | 20 | >95 | – | 42 | 62:38 | 3 |
| 10 | AuCl(Me$_2$S) | 84 | >95 | – | 46 | 45:55 | 5 |
| 11[e] | AuPicCl$_2$[j] | 20 | >95 | – | 21 | 50:50 | 14 |
| 12[f] | AuPicCl$_2$[j] | 84 | >95 | – | 14 | 40:60 | 18 |
| 13[g] | AuCl$_3$(Pyridine)[j] | 20 | >95 | – | 25 | 60:40 | 35 |
| 14[h] | AuCl$_3$(Pyridine)[j] | 84 | >95 | – | 18 | 45:55 | 39 |

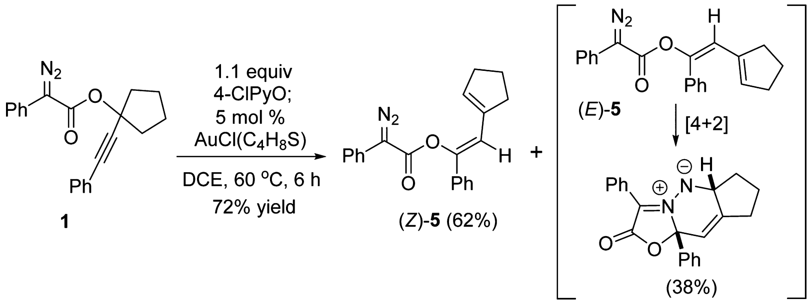
[a] Reactions were performed on a 0.10 mmol scale: a solution of **1** (0.10 mmol) in DCE (1.0 mL) was added to a solution of Au catalyst (5 mol %) in DCE (1.0 mL) under a nitrogen atmosphere at 20 °C (% conversion in parentheses for entries 1−6) or in refluxing DCE, and the resulting reaction mixture was stirred for defined periods of time. [b] Conversion of **1**, yields of **2**, (**3** + **4**), **5**, and ratios **3**:**4** were determined by $^1$H NMR analysis of characteristic peaks using 2,4,6-trimethoxybenzene as the internal standard. Reaction times were 72 h for the reactions carried out at 20 °C, and 6 h at 84 °C. [c] Reaction time: 12 h. [d] Reaction time: 48 h. [e] Yield of product **6**: 24%. [f] Yield of product **6**: 27%. [g] Yield of product **6**: 32%. [h] Yield of product **6**: 38%. [i] At 50 °C after 12 h: 81% yield of **3** + **4** with **3**:**4** = 40:60. [j] Reduction of the catalyst to elemental gold is significant.

Scheme 4. Proposed Mechanism for the Formation of **10**, **11**, and **12** from **9**



DOI: 10.1021/acs.joc.6b01833
J. Org. Chem. 2016, 81, 9235−9246

**Scheme 5. Role of the Pyridine-*N*-oxide in Diene Formation from Phenylpropargyl Phenyldiazoacetate 1**



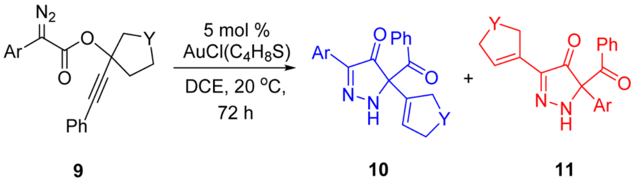
initially from **A** and undergoes acyl migration to reach equilibrium with **11**. This mechanism explains the formation of **10** from carboxyallene **C**, the equilibrium that exists between **10** and **11**, and the formation of only (*Z*)-diene **12** from **A** through **B** without evidence for the formation of the isomeric (*E*)-diene that was reported when the same reaction is performed in the presence of 4-chloropyridine-*N*-oxide.[10,15]

The formation of **12** is consistent with the results reported for the rearrangement of an acetate analogue of **1**,[9c] and the conversion of **B** to **12** is consistent with the formation of diene **12** as the sole geometrical isomer. The difference between the two pathways for diene formation (in the presence and absence of pyridine-*N*-oxide) is that the pyridine-*N*-oxide intercepts activated allene **A** as a base to form both (*E*)- and (*Z*)-**12**, whereas, without the added base, **B** is formed and undergoes intramolecular proton transfer to form the observed (*Z*)-**12**.

Although diazo compounds are normally regarded as nucleophiles, with both the diazo carbon and the terminal nitrogen as nucleophilic centers,[16] there are examples in which the terminal nitrogen atom of diazo compounds exhibits electrophilic reactivity.[14b,17] These reactions are intermolecular and involve obvious nucleophilic attack on the terminal nitrogen of diazocarbonyl compounds and result in the formation of hydrazone derivatives. The formation of **10** can be considered to be initiated by intramolecular electrophilic addition of the *N*-terminus of the aryldiazoacetates onto the central carbon of the allene that is continued with hydrogen transfer and C4−C2 bond formation, which occurs with the release of the Ar$_2$CO acyl group. To confirm that the allene forms both (*Z*)- and (*E*)-dienes with a pyridine-*N*-oxide, the latter undergoing [4 + 2]-cycloaddition,[10] propargyl phenyldiazoacetate **1** was combined with 1.1 equiv of 4-chloropyridine-*N*-oxide and heated at 60 °C in the presence of 5 mol % AuCl(C$_4$H$_8$S) for 6 h. Allene formation was observed prior to addition of 4-chloropyridine-*N*-oxide, and both the (*Z*)-diene **5** and the cycloaddition product from the (*E*)-diene were the sole reaction products (Scheme 5). Diene formation is not observed in the absence of gold(I) catalyst, but with only 20 mol % of 4-chloropyridine-*N*-oxide, all four products (**3**, **4**, (*Z*)-**5**, and (*E*)-**5**) were obtained from the reaction performed with 5 mol % AuCl(C$_4$H$_8$S) at 60 °C for 6 h.[18]

**Substrate Scope.** The substrate scope of phenylpropargyl aryldiazoacetates **9a**−**k** (Table 2) demonstrates that the AuCl(C$_4$H$_8$S)-catalyzed reaction is broadly appropriate for the synthesis of the 1,5-dihydro-4*H*-pyrazol-4-ones **10** and **11**, and these reactions are tolerant of both electron-donating and electron-withdrawing substituents in the aryl group of the aryldiazoacetate. High total yields of the **10** + **11** composites are observed, and their **10**:**11** ratio is near 3:1 (Table 2). Substrate **9j** with a 12-membered ring gives a high yield of the **10j** + **11j** composite, but its **10**:**11** ratio is 3:2. Tetrahydropyranyl derivatives **10k** + **11k** are obtained in only 46% yield and a 78:22 **10**:**11** ratio.

**Table 2. Substrate Scope of Gold(I)-Catalyzed Reaction of Phenylpropargyl Aryldiazoacetates 9**[a]



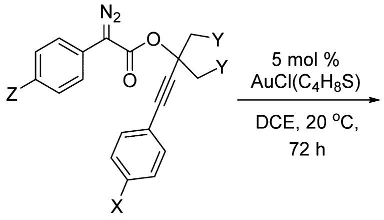
| 9−11 | Ar (Y = CH$_2$) | yield (%)[b,c] | ratio **10**:**11**[b] |
|---|---|---|---|
| a | C$_6$H$_5$ | 76 | 75:25 |
| b | *p*-MeO-C$_6$H$_4$ | 75 | 72:28 |
| c | *p*-Me-C$_6$H$_4$ | 85 | 72:28 |
| d | *p*-Ph-C$_6$H$_4$ | 78 | 88:12 |
| e | *p*-Br-C$_6$H$_4$ | 87 | 85:15 |
| f | *p*-Cl-C$_6$H$_4$ | 83 | 83:17 |
| g | *p*-CF$_3$-C$_6$H$_4$ | 73 | 70:30 |
| h | 2-C$_4$H$_3$S[d] | 67 | 88:12 |
| **9−11** | **Y (Ar = C$_6$H$_5$)** | **yield (%)[b,c]** | **ratio 10:11[b]** |
| i | (CH$_2$)$_2$ | 73 | 78:22 |
| j | (CH$_2$)$_8$ | 86 | 59:41 |
| k | CH$_2$O | 46 | 78:22 |

[a]Reactions were carried out at 20 °C on a 0.20 mmol scale: a solution of **1** in 2.0 mL DCE was added to a 5 mol % solution of AuCl(C$_4$H$_8$S) in 2.0 mL of DCE under a nitrogen atmosphere, and the resulting reaction mixture was stirred for 72 h. [b]Ratios and yields were determined by $^1$H NMR spectroscopy using 2,4,6-trimethoxybenzaldehyde as the internal standard. [c]Individual compounds **10** and **11** were isolated and fully characterized (see the Experimental Section and the SI). [d]2-C$_4$H$_3$S = 2-Thiophene.

With substrates having electron-withdrawing or electron-donating groups (EWG or EDG) in both arene nuclei, the product outcome is quite similar (Scheme 6) to those presented in Table 2. However, having an EWG as Z and an EDG as X (compound **9o**) results in a lower yield of **10o** + **11o** (47%) but a higher **10**:**11** ratio of 89:11. High yield (79%) and almost exclusive formation of compound **10q** (**10**:**11** = 91:9) are observed from the dimethyl analogue **9q**, whereas aryl unsubstituted analogue **9p** results in lower yield of **10p** + **11p** (68%) with an 88:12 **10**:**11** ratio.

The cyclobutyl analogue **9r** (Scheme 7) forms neither **10** nor **11**. Instead, treatment of **9r** with 5 mol % AuCl(C$_4$H$_8$S) affords **13** in good yield (70%), but only at 80 °C over 12 h. This product is consistent with initial formation of a gold-carbene intermediate through the diazo functional group. The alternate pathway through a strained allene intermediate is apparently

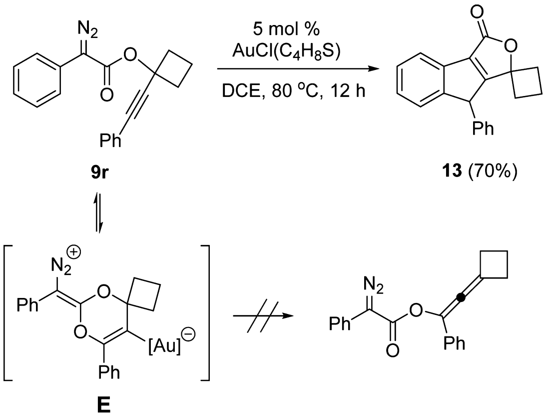
Scheme 6. Substrate Scope of Gold(I)-Catalyzed Reaction of Arylpropargyl Aryldiazoacetates 9



**9**

| 10,11 | X | Y | Z | Yield (%) | 10:11 |
|---|---|---|---|---|---|
| l | Cl | $CH_2$ | H | 80 | 77:23 |
| m | OMe | $CH_2$ | H | 77 | 62:38 |
| n | OMe | $CH_2$ | OMe | 79 | 70:30 |
| o | OMe | $CH_2$ | $CF_3$ | 47 | 89:11 |
| p | H | H | H | 68 | 88:12 |
| q | H | H | OMe | 79 | 91:9 |

Scheme 7. Outcome of Gold(I)-Catalyzed Reaction of Cyclobutyl Propargyl Reactant 9r



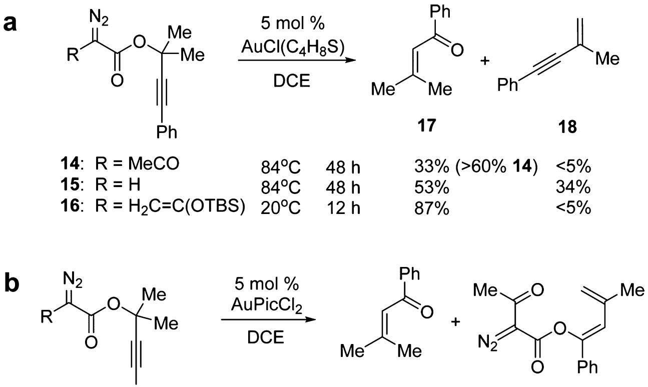
too restrictive and, although the initial step in the 1,3-acyl rearrangement that produces the stabilized intermediate **E** is favorable, release of the C−O bond to form the allene does not occur.

**Diazoacetate Influence.** The conversion of **A** to **10** in Scheme 4 was expected to be dependent on the relative basicity of the ester carbonyl for 1,3-acyl transfer and the relative electrophilicity of the diazo terminal nitrogen for rearrangement. To evaluate these dependencies, we prepared acceptor and acceptor−acceptor analogues (**14** and **15**) of the donor−acceptor phenylpropargyl aryldiazoacetate **9**, as well as another donor−acceptor diazo compound **16**, and performed gold-catalyzed reactions with them (Scheme 8a,b) under the same conditions as those performed with **1** (see Table 1).

In all cases, the allene intermediate was formed and reached equilibrium within 5 min, but the rearrangement product **22** was not observed (Scheme 9). In contrast to reactions with propargyl aryldiazoacetates **1** or **9**, however, both **14** and **15** were unreactive with $\mathrm{AuCl(C_4H_8S)}$ at room temperature but in refluxing 1,2-dichloroethane underwent cleavage to form enone **17** (Scheme 8a), whose formation is consistent with the pathway through intermediate **B** in Scheme 4 (equivalent to **F** in Scheme 9), and with **18**, the acid-catalyzed elimination product for which the diazoacetic acid is the leaving group. The absence of rearranged product **22** in reactions with **14** or **15** can be attributed to the diminished electrophilicity of their diazo terminal nitrogens, but the facility with which donor−acceptor diazo compound **16** forms cleavage product **17** instead of **22** is possibly related to other factors.

With the gold(III) catalyst $\mathrm{AuPicCl_2}$, the same reactions occurred with diazo compounds **14**−**16** (Scheme 8b) but at lower temperatures and, except for **14**, gave the same products as with $\mathrm{AuCl(C_4H_8S)}$. Diazoacetoacetate **14** gave diene **21** as the major product whose formation through intermediate **F** occurs in competition with the production of cleavage product **17**. Once again, the rearranged product **22** or its acyl transfer product is absent in the product mixture, suggesting the uniqueness of the overall process that forms **22** and its analogues.

Scheme 8. (a) Product Dependence on Diazo Compound Catalyzed by $\mathrm{AuCl(C_4H_8S)}$. (b) Product Dependence on Diazo Compound Catalyzed by $\mathrm{AuPicCl_2}$



| | | | 17 | 18 |
|---|---|---|---|---|
| **14**: R = MeCO | 84°C | 48 h | 33% (>60% **14**) | <5% |
| **15**: R = H | 84°C | 48 h | 53% | 34% |
| **16**: R = H₂C=C(OTBS) | 20°C | 12 h | 87% | <5% |

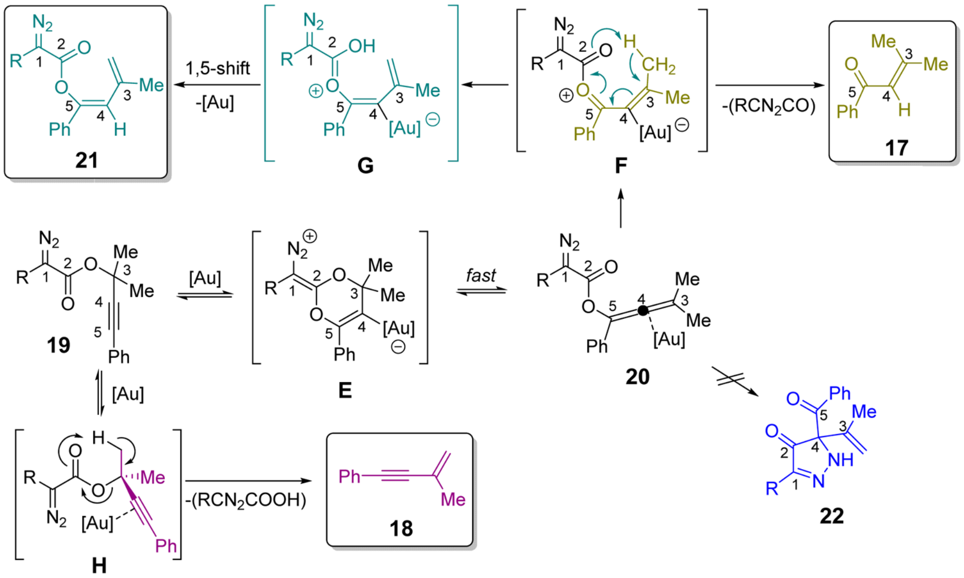
| | | | 17 (18) | 21 |
|---|---|---|---|---|
| **14**: R = MeCO | 40°C | 12 h | 14% (<5%) | 82% |
| **15**: R = H | 20°C | 12 h | 72% (17%) | – |
| **16**: R = H₂C=C(OTBS) | 20°C | 12 h | 76% (<5%) | – |

## ■ CONCLUSION

We have discovered a unique gold(I)-catalyzed rearrangement of propargyl aryldiazoacetates and a platform on which catalytic activity of gold complexes can be assessed. Arylpropargyl aryldiazoacetates have two reactive sites for reactions with gold complexes. If initial interaction occurs at the diazo carbon, a gold carbene is the outcome, and a subsequent cascade process results in the formation of a product that is uniquely characteristic of this pathway. If gold coordination occurs with the carbon−carbon triple bond, 1,3-acyloxy migration of the propargylic ester promoted by the diazoester takes place. The corresponding allene formed rapidly is a stable intermediate, and it determines the course of subsequent processes, one of which is to undergo gold-catalyzed formation of a gold-acylacylium ion intermediate to form stable products by cleavage or intramolecular hydrogen migration. Alternatively, the allene intermediate undergoes a complex transformation, not catalyzed by gold, in which the terminal nitrogen of the diazo functional group adds at the central carbon of the allene to initiate a sequence of bond-forming reactions, resulting in the production of 1,5-dihydro-4*H*-pyrazol-4-ones in good yields. As acyl transfer agents, these unique products undergo intramolecular 1,3-acyl migration to form an

DOI: 10.1021/acs.joc.6b01833
*J. Org. Chem.* 2016, 81, 9235−9246

Scheme 9. Diazo Compound Alternate Pathways to Product Formation



equilibrium mixture of two isomeric 1,5-dihydro-4*H*-pyrazol-4-ones under the reaction conditions or quantitatively transfer the acyl group to an external nucleophile with formation of 4-hydroxypyrazoles. Cationic gold(I) complexes initiate their reactions at room temperature exclusively with the diazo functional group of propargyl phenyldiazoacetates, whereas both AuCl(R$_2$S) and gold(III) catalysts undergo initial reaction exclusively at the carbon−carbon triple bond. Neutral gold(I) chloride complexes having strongly coordinating ligands show very low or negligible conversion of propargyl phenyldiazoacetates at room temperature, but they undergo slow reaction at higher temperatures to give mainly the product from reaction at the diazo functional group, which may have occurred after chloride dissociation,[2c] sometimes in competition with products from reaction at the carbon−carbon triple bond.

## ■ EXPERIMENTAL SECTION

**General Information.** All reactions were carried out under an atmosphere of dry nitrogen in oven-dried glassware using freshly distilled solvents. All solvents were purified and dried using standard techniques. Thin layer chromatography (TLC) analyses were performed on precoated analytical plates Silica Gel 60 F$_{254}$, and visualized with the use of UV light or iodine stain (I$_2$ and Silica Gel 60). High-resolution mass spectra (HRMS) were performed on a microTOF-ESI mass spectrometer. Exact masses were reported for the molecular ions [M + Na]$^+$, [M + H]$^+$, or [M − H]$^-$. Column chromatography was performed on a CombiFlash purification system using normal phase disposable columns. IR spectra were recorded using an FT-IR spectrometer. NMR spectra were recorded on spectrometers at 300, 400, or 500 MHz ($^1$H NMR) and 76, 100, or 126 MHz ($^{13}$C NMR). Chemical shifts are reported in ppm using residue CHCl$_3$ ($\delta$ 7.26 ppm)/H$_2$O ($\delta$ 1.56 ppm), CH$_3$OH ($\delta$ 3.31 ppm)/H$_2$O ($\delta$ 4.87 ppm), DMSO ($\delta$ 2.50 ppm)/H$_2$O ($\delta$ 3.33 ppm) for $^1$H NMR reference and the central resonance of CDCl$_3$ ($\delta$ 77.16 ppm), CD$_3$OD ($\delta$ 49.00 ppm), DMSO-d6 ($\delta$ 39.52 ppm) for $^{13}$C NMR reference. $^1$H NMR spectra are reported as follows (s = singlet, br = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = unresolved multiplet, comp = composite of magnetically non-equivalent protons); coupling constants (*J*) are given in hertz (Hz).

**Materials.** AuCl(PPh$_3$), AuCl(PMe$_3$), AuCl[P(OMe)$_3$], chloro[2-dicyclohexyl(2′,6′-dimethoxybiphenyl)phosphine]-gold(I), AuPicCl$_2$, AuCl(C$_4$H$_8$S), AuCl(Me$_2$S), AuCl(CO), (IPr)AuCl, and AuCl$_3$(Py) were purchased from commercial suppliers. All other chemicals were obtained from commercial sources and used as received without further purification.

**Characterization of Propargyl Diazoacetates.** Detailed procedures for the preparation of diazo compounds **9** and characterization data of compounds **1** (**9a**), **9c**−**g**, **9l**, and **m** were previously reported.[10] The reactions were carried out on a 5 mmol scale; reported are total yields of two steps: DCC coupling and diazo transfer.

*1-(Phenylethynyl)cyclopentyl 2-Diazo-2-(4-methoxyphenyl)-acetate (**9b**).* 1.24 g, 69% yield. Orange oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49−7.44 (comp, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.33−7.28 (comp, 3H), 6.95 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 2.42 (ddd, *J* = 12.3, 7.8, 3.7 Hz, 2H), 2.35−2.26 (comp, 2H), 1.90−1.78 (comp, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 164.1, 158.0, 131.8, 128.3, 128.1, 125.9, 122.7, 117.1, 114.6, 89.5, 85.0, 82.0, 55.4, 40.8, 23.5. IR (neat) 2954, 2075, 1702, 1512, 1255, 1145, 997 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for C$_{22}$H$_{20}$N$_2$O$_3$Na [M + Na]$^+$ 383.1366, found: 383.1361.

*1-(Phenylethynyl)cyclopentyl 2-Diazo-2-(thiophen-2-yl)acetate (**9h**).* 874 mg, 52% yield. Dark-red oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.34−7.28 (m, 4H), 7.07−7.03 (m, 1H), 6.84 (d, *J* = 3.6 Hz, 1H), 2.49−2.41 (m, 2H), 2.31 (dt, *J* = 15.3, 7.7 Hz, 2H), 1.87−1.81 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.4, 131.9, 128.3, 128.1, 126.9, 125.9, 125.4, 122.6, 120.9, 89.0, 85.3, 82.9, 40.8, 23.4. IR (neat) 2928, 2076, 1701, 1443, 1285, 1231, 1127, 974, 691 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for C$_{19}$H$_{16}$N$_2$O$_2$SNa [M + Na]$^+$ 359.0825, found: 359.0822.

*1-(Phenylethynyl)cyclohexyl 2-Diazo-2-phenylacetate (**9i**).* 1.14 g, 66% yield. Yellow solid, mp 50−51 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.53 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.50−7.45 (comp, 2H), 7.42−7.36 (comp, 2H), 7.34−7.28 (comp, 3H), 7.21−7.16 (m, 1H), 2.36−2.21 (comp, 2H), 2.09 (comp, 2H), 1.81−1.65 (comp, 4H), 1.62−1.53 (m, 1H), 1.45 (ddd, *J* = 13.1, 8.5, 4.8 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.1, 131.9, 128.9, 128.3, 128.1, 125.8, 125.7, 124.0, 122.7, 89.1, 86.5, 77.1, 37.5, 25.2, 22.7. IR (neat) 2936, 2083, 1707, 1241, 754, 691 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for C$_{22}$H$_{20}$N$_2$O$_2$Na [M + Na]$^+$ 367.1417, found: 367.1410.

*1-(Phenylethynyl)cyclododecyl 2-Diazo-2-phenylacetate (**9j**).* 1.33 g, 62% yield. Yellow solid, mp 92.5−93.5 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.53 (dd, *J* = 7.6, 0.9 Hz, 2H), 7.50−7.44 (comp, 2H), 7.42−7.35 (comp, 2H), 7.34−7.27 (comp, 3H), 7.19 (ddd, *J* = 8.6, 2.2, 1.1 Hz, 1H), 2.37−2.23 (comp, 2H), 2.12−1.98 (comp, 2H), 1.68 (d, *J* = 8.8 Hz, 2H), 1.43 (comp, 16H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.1, 131.9, 128.9, 128.3, 128.1, 125.8, 125.7, 124.0, 122.7, 89.4, 86.2, 79.6, 33.4, 26.1, 25.9, 22.3, 22.1, 19.4. IR (neat) 2928, 2079, 1705, 1470, 1241, 1146, 1006, 754 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for C$_{28}$H$_{32}$N$_2$O$_2$Na [M + Na]$^+$ 451.2356, found: 451.2343.

DOI: 10.1021/acs.joc.6b01833
*J. Org. Chem.* 2016, 81, 9235−9246

*4-(Phenylethynyl)tetrahydro-2H-pyran-4-yl 2-Diazo-2-phenylacetate (**9k**).* 1.12 g, 65% yield. Yellow solid, mp 85−86 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.57−7.45 (comp, 4H), 7.44−7.36 (comp, 2H), 7.36−7.28 (comp, 3H), 7.23−7.17 (m, 1H), 3.93 (dt, *J* = 9.2, 4.4 Hz, 2H), 3.85 (ddd, *J* = 11.9, 9.0, 2.9 Hz, 2H), 2.45−2.38 (comp, 2H), 2.23 (ddd, *J* = 13.1, 9.0, 4.0 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.0, 131.9, 128.9, 128.7, 128.2, 125.9, 125.4, 124.1, 122.2, 87.5, 87.5, 74.1, 64.5, 38.0. IR (neat) 2960, 2086, 1707, 1498, 1241, 1140, 755 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{18}N_2O_3Na$ [M + Na]$^+$ 369.1214, found: 369.1210.

*1-((4-Methoxyphenyl)ethynyl)cyclopentyl 2-Diazo-2-(4-methoxyphenyl)acetate (**9n**).* 1.13 g, 58% yield. Orange oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 10.1, 9.0 Hz, 4H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 2.46−2.37 (m, 2H), 2.34−2.24 (m, 2H), 1.87−1.78 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.1, 159.6, 158.0, 133.3, 125.9, 117.1, 114.8, 114.5, 113.8, 88.1, 84.9, 82.3, 55.34, 55.25, 40.8, 23.5. IR (neat) 2956, 2080, 1703, 1511, 1248, 1147, 830, 734 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{23}H_{22}N_2O_4Na$ [M + Na]$^+$ 413.1472, found: 413.1483.

*1-((4-Methoxyphenyl)ethynyl)cyclopentyl 2-Diazo-2-[(4-(trifluoromethyl)phenyl]acetate (**9o**).* 1.18 g, 55% yield. Orange oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72−7.52 (comp, 4H), 7.40 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.50−2.37 (comp, 2H), 2.37−2.22 (comp, 2H), 1.85 (comp, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.8, 159.7, 133.3, 130.3, 127.5 (q, *J* = 32.5 Hz), 125.7 (q, *J* = 3.8 Hz), 123.5, 114.6, 113.8, 87.6, 85.3, 82.9, 77.3, 77.0, 76.8, 55.3, 40.8, 23.4. IR (neat) 2957, 2087, 1706, 1509, 1323, 1244, 1070, 832 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{23}H_{19}F_3N_2O_3Na$ [M + Na]$^+$ 451.1240, found: 451.1225.

*2-Methyl-4-phenylbut-3-yn-2-yl 2-Diazo-2-phenylacetate (**9p**).* 958 mg, 63% yield. Orange oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.53−7.43 (comp, 4H), 7.41−7.35 (comp, 2H), 7.32−7.27 (comp, 3H), 7.21−7.14 (m, 1H), 1.85 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.4, 131.9, 128.9, 128.4, 128.2, 125.7, 125.7, 124.0, 122.5, 90.0, 84.5, 73.8, 29.4. IR (neat) 2936, 2079, 1705, 1498, 1349, 1247, 1120, 754, 691 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{19}H_{16}N_2O_2Na$ [M + Na]$^+$ 327.1104, found: 327.1102.

*2-Methyl-4-phenylbut-3-yn-2-yl 2-Diazo-2-(4-methoxyphenyl)acetate (**7** or **9q**).* 1.14 g, 68% yield. Orange oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.49−7.44 (comp, 2H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.34−7.28 (comp, 3H), 6.95 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 1.85 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.9, 158.0, 131.9, 128.4, 128.1, 126.0, 122.6, 117.2, 114.6, 90.1, 84.4, 73.7, 55.4, 29.5. IR (neat) 2988, 2079, 1705, 1514, 1258, 1122, 998, 827 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{20}H_{18}N_2O_3Na$ [M + Na]$^+$ 357.1210, found: 357.1209.

*1-(Phenylethynyl)cyclobutyl 2-Diazo-2-phenylacetate (**9r**).* 822 mg, 52% yield. Yellow solid, mp 76−77 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.50−7.45 (comp, 2H), 7.42−7.36 (comp, 2H), 7.34−7.29 (comp, 3H), 7.23−7.16 (m, 1H), 2.81−2.71 (comp, 2H), 2.62 (ddd, *J* = 12.7, 9.8, 2.6 Hz, 2H), 2.15−2.05 (m, 1H), 2.00 (ddd, *J* = 9.8, 8.6, 4.9 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.2, 131.9, 128.9, 128.4, 128.2, 125.8, 125.5, 124.0, 122.5, 89.2, 84.8, 73.3, 37.2, 14.7. IR (neat) 2952, 2081, 1704, 1497, 1351, 1242, 1144, 1088, 754, 691 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{20}H_{16}N_2O_2Na$ [M + Na]$^+$ 339.1104, found: 339.1107.

*2-Methyl-4-phenylbut-3-yn-2-yl 2-Diazo-3-oxobutanoate (**14**).* Prepared according to the general procedure[1] from acetoacetic acid; 797 mg, 59% yield. Pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.49−7.40 (comp, 2H), 7.35−7.27 (comp, 3H), 2.49 (s, 3H), 1.83 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 190.3, 159.6, 131.8, 128.6, 128.2, 122.2, 89.2, 85.0, 74.7, 29.4, 28.3. IR (neat) 2988, 2137, 1719, 1655, 1315, 1121, 1058, 693 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{15}H_{14}N_2O_3Na$ [M + Na]$^+$ 293.0897, found: 293.0891.

*2-Methyl-4-phenylbut-3-yn-2-yl 2-Diazoacetate (**15**).* Prepared according to literature procedure[7e] for the related diazo compounds; 524 mg, 46% total yield. Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 8.2, 3.7 Hz, 2H), 7.30 (dd, *J* = 4.7, 2.3 Hz, 3H), 4.72 (s, 1H), 1.80 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 131.8, 128.4, 128.1, 122.5, 90.1, 84.2, 73.5, 46.7, 29.4. IR (neat) 2987, 2111, 1701, 1370, 1186, 1124, 983, 693 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{13}H_{12}N_2O_2Na$ [M + Na]$^+$ 251.0791, found: 251.0798.

*2-Methyl-4-phenylbut-3-yn-2-yl 3-(tert-Butyldimethylsilyl)oxy-2-diazo-but-3-enoate (**16**).* Synthesized according to the published procedure[19] from compound **14**; 1.67 g, 88% yield. Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.48−7.43 (comp, 2H), 7.34−7.28 (comp, 3H), 5.03 (d, *J* = 2.1 Hz, 1H), 4.26 (d, *J* = 2.1 Hz, 1H), 1.81 (s, 6H), 0.93 (s, 9H), 0.24 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.5, 140.9, 131.8, 128.4, 128.1, 122.5, 90.4, 89.9, 84.4, 73.6, 29.4, 25.6, 18.1, − 4.8. IR (neat) 2956, 2088, 1715, 1342, 1255, 1057, 842 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{28}N_2O_3SiNa$ [M + Na]$^+$ 407.1761, found: 407.1745.

**General Procedure for Gold(I)-Catalyzed Domino Cascade Transformation of Phenylpropargyl Phenyldiazoacetates.** To a flame-dried 10 mL Schlenk flask charged with a magnetic stirring bar were added cationic gold(I) catalyst (0.010 mmol) and 2.0 mL of DCM under a nitrogen atmosphere. 1-(Phenylethynyl)cyclopentyl 2-diazo-2-phenylacetate **1** (0.20 mmol) dissolved in 2.0 mL of DCM was added in one portion into the solution under the flow of nitrogen. The resulting mixture was stirred for 12 h at room temperature (20 °C); the reaction mixture was purified by column chromatography (100:1 to 10:1 gradient of hexanes:ethyl acetate as eluents) to afford pure *8′-phenylspiro[cyclopentane-1,1′-indeno[1,2-c]furan]-3′(8′H)-one* (**2**) as a white solid (52 mg, 86% using catalyst [Au(JohnPhos)(MeCN)]-$SbF_6$); mp 128−129 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.40−7.36 (m, 1H), 7.33−7.30 (comp, 3H), 7.27−7.24 (comp, 2H), 7.08−7.06 (comp, 2H), 4.80 (s, 1H), 2.11−2.08 (comp, 2H), 2.07−2.02, (m, 1H), 2.01−1.98 (m, 1H), 1.98−1.82 (m, 1H), 1.81−1.69 (m, 1H), 1.67−1.55 (m, 1H), 1.33−1.25 (m, 1H); $^{13}$C NMR (400 MHz, $CDCl_3$) δ 179.0, 166.4, 152.0, 136.1, 135.9, 134.3, 129.1, 128.1, 127.9, 127.7, 125.0, 120.9, 95.5, 52.4, 38.5, 36.7, 24.4. IR (neat) 2961, 1751, 1453, 1090, 953, 771 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{18}O_2Na$ [M + Na]$^+$ 325.1199, found: 325.1200.

*8′-Phenylspiro[cyclobutane-1,1′-indeno[1,2-c]furan]-3′(8′H)-one (**13**).* Obtained using 5 mol % of Au($C_4H_8S$)Cl at 80 °C in DCE for 12 h: 40.3 mg, 70% yield. White solid, mp 150−151 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.38−7.32 (comp, 4H), 7.27−7.21 (comp, 2H), 7.15−7.13 (comp, 2H), 4.89 (s, 1H), 2.82−2.74 (m, 1H), 2.51−2.47 (comp, 2H), 1.84−1.73 (comp, 2H), 1.60−1.50 (m, 1H); $^{13}$C NMR (400 MHz, $CDCl_3$) δ 178.2, 166.2, 152.2, 135.8, 135.5, 133.8, 129.0, 128.1, 127.9, 127.0, 125.0, 120.9, 85.9, 52.4, 33.3, 31.7, 12.2. IR (neat) 1756, 1454, 1154, 1066, 991, 722, 700 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{20}H_{16}O_2Na$ [M + Na]$^+$ 311.1043, found: 311.1050.

**General Procedure for the Synthesis of 1,5-Dihydro-4*H*-pyrazol-4-ones 10 and 11.** To a flame-dried 10 mL Schlenk flask charged with a magnetic stirring bar were added AuCl($C_4H_8S$) catalyst (0.010 mmol) and 2.0 mL of DCE under a nitrogen atmosphere. Propargyl aryldiazoacetate **1** or **9** (0.20 mmol) dissolved in 2.0 mL of DCE was added in one portion into the solution under the flow of nitrogen. The resulting mixture was stirred for 72 h at room temperature (20 °C). Solvent was evaporated, and products were purified by column chromatography (100:1 to 10:1 gradient of hexanes:ethyl acetate as eluents) to afford pure compounds **10** and **11**.

*5-Benzoyl-5-(cyclopent-1-en-1-yl)-3-phenyl-1,5-dihydro-4H-pyrazol-4-one (**3** or**10a**).* 37.6 mg, 57% yield. Yellow solid, mp 115−116 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.9, 1.2 Hz, 2H), 8.08 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.90 (br, 1H), 7.62−7.57 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.42−7.36 (comp, 3H), 5.88−5.84 (m, 1H), 2.50−2.41 (comp, 3H), 2.35−2.29 (m, 1H), 1.98−1.89 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 192.1, 189.7, 143.8, 138.5, 134.0, 133.4, 131.6, 130.7, 129.2, 129.1, 128.5, 128.4, 126.0, 81.5, 32.4, 32.4, 23.0. IR (neat) 3358, 1721, 1674, 1246, 903 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{18}N_2O_2Na$ [M + Na]$^+$ 353.1260, found: 353.1247.

*5-Benzoyl-3-(cyclopent-1-en-1-yl)-5-phenyl-1,5-dihydro-4H-pyrazol-4-one (**4** or **11a**).* 12.5 mg, 19% yield. Yellow solid, mp 130−131 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.66 (br, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42−7.33 (comp, 7H), 6.84−6.80 (m, 1H), 2.75−2.70 (comp, 2H), 2.56−2.49 (comp, 2H), 1.96−1.89 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 192.7, 189.5, 143.2, 135.7, 134.1, 133.7, 133.1, 132.0, 130.9, 129.5, 128.8, 128.5, 126.5, 81.8, 34.1, 32.7, 22.2. IR (neat) 3343, 1732, 1675, 1447, 1231, 738 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{18}N_2O_2Na$ [M + Na]$^+$ 353.1260, found: 353.1249.

*5-Benzoyl-5-(cyclopent-1-en-1-yl)-3-(4-methoxyphenyl)-1,5-dihydro-4H-pyrazol-4-one (**10b**).* 36.3 mg, 54% yield. Yellow solid, mp 44−46 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.18 (d, $J$ = 7.3 Hz, 2H), 8.03 (d, $J$ = 9.0 Hz, 2H), 7.73 (s, 1H), 7.62−7.56 (m, 1H), 7.50−7.44 (comp, 2H), 6.92 (d, $J$ = 9.0 Hz, 2H), 5.87−5.82 (m, 1H), 3.84 (s, 3H), 2.52−2.39 (comp, 3H), 2.31 (dddd, $J$ = 17.5, 9.3, 5.8, 2.1 Hz, 1H), 2.02−1.84 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.5, 189.9, 160.5, 144.2, 138.7, 133.9, 133.5, 131.4, 130.7, 128.3, 127.6, 121.7, 114.0, 81.3, 55.3, 32.5, 32.4, 23.0. IR (neat) 3338, 2931, 1712, 1674, 1608, 1510, 1251, 1176, 835 cm$^{-1}$; HRMS (EI) *m*/*z* calculated for $C_{22}H_{19}N_2O_3$ [M − H]$^-$ 359.1401, found: 359.1396.

*5-Benzoyl-3-(cyclopent-1-en-1-yl)-5-(4-methoxyphenyl)-1,5-dihydro-4H-pyrazol-4-one (**11b**).* 14.1 mg, 21% yield. Yellow solid, mp 60.5−61.5 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 8.5 Hz, 2H), 7.73 (s, 1H), 7.53−7.47 (m, 1H), 7.36 (dd, $J$ = 11.7, 4.0 Hz, 2H), 7.26 (d, $J$ = 7.8 Hz, 2H), 6.92 (d, $J$ = 7.8 Hz, 2H), 6.82−6.81 (m, 1H), 3.80 (s, 3H), 2.76−2.68 (m, 2H), 2.52 (d, $J$ = 5.6 Hz, 2H), 1.96−1.88 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 193.1, 189.7, 159.8, 143.2, 133.9, 133.6, 133.1, 132.1, 131.0, 128.4, 127.9, 127.8, 114.9, 81.6, 55.3, 34.1, 32.7, 22.2. IR (neat) 3344, 2954, 1736, 1673, 1608, 1510, 1252, 692 cm$^{-1}$; HRMS (EI) *m*/*z* calculated for $C_{22}H_{19}N_2O_3$ [M − H]$^-$ 359.1401, found: 359.1406.

*5-Benzoyl-5-(cyclopent-1-en-1-yl)-3-(p-tolyl)-1,5-dihydro-4H-pyrazol-4-one (**10c**).* 42.0 mg, 61% yield. Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.19−8.14 (comp, 2H), 7.97−7.92 (comp, 2H), 7.78 (s, 1H), 7.60−7.56 (m, 1H), 7.47−7.43 (comp, 2H), 7.21−7.18 (comp, 2H), 5.85−5.82 (m, 1H), 2.46−2.38 (comp, 3H), 2.36 (s, 3H), 2.31−2.26 (m, 1H), 1.96−1.88 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.3, 189.8, 144.2, 139.3, 138.6, 134.0, 133.5, 131.5, 130.7, 129.2, 128.4, 128.3, 126.0, 81.4, 32.5, 32.4, 23.0, 21.4. IR (neat) 3344, 1722, 1676, 1231, 951 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{22}H_{20}N_2O_2Na$ [M + Na]$^+$ 367.1417, found: 367.1404.

*5-Benzoyl-3-(cyclopent-1-en-1-yl)-5-(p-tolyl)-1,5-dihydro-4H-pyrazol-4-one (**11c**).* 16.5 mg, 24% yield. Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.88−7.80 (comp, 2H), 7.67 (s, 1H), 7.51−7.47 (m, 1H), 7.37−7.32 (comp, 2H), 7.24−7.16 (comp, 4H), 6.83−6.78 (m, 1H), 2.74−2.68 (comp, 2H), 2.55−2.48 (comp, 2H), 2.34 (s, 3H), 1.96−1.88 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.9, 189.6, 143.2, 138.8, 133.9, 133.7, 133.1, 132.9, 132.0, 131.0, 130.2, 128.4, 126.4, 81.8, 34.1, 32.7, 22.2, 21.1. IR (neat) 3348, 1737, 1675, 1230, 809 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{22}H_{20}N_2O_2Na$ [M + Na]$^+$ 367.1417, found: 367.1407.

*3-([1,1′-Biphenyl]-4-yl)-5-benzoyl-5-(cyclopent-1-en-1-yl)-1,5-dihydro-4H-pyrazol-4-one (**10d**).* 56.0 mg, 69% yield. Yellow solid, mp 49−51 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.23−8.15 (comp, 2H), 7.98 (s, 1H), 7.68−7.58 (comp, 6H), 7.47 (dt, $J$ = 12.5, 7.9 Hz, 5H), 7.37 (t, $J$ = 7.4 Hz, 1H), 5.89 (m, 1H), 2.59−2.40 (comp, 3H), 2.35 (ddd, $J$ = 15.2, 11.0, 4.0 Hz, 1H), 2.04−1.86 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.1, 189.8, 143.5, 141.8, 140.5, 138.5, 134.0, 133.5, 131.7, 130.7, 128.8, 128.4, 128.1, 127.6, 127.2, 127.0, 126.4, 81.6, 32.5, 23.0. IR (neat) 3346, 2957, 1725, 1674, 1233, 907, 733 cm$^{-1}$; HRMS (EI) *m*/*z* calculated for $C_{27}H_{21}N_2O_2$ [M − H]$^-$ 405.1609, found: 405.1610.

*5-([1,1′-Biphenyl]-4-yl)-5-benzoyl-3-(cyclopent-1-en-1-yl)-1,5-dihydro-4H-pyrazol-4-one (**11d**).* 7.3 mg, 9% yield. Yellow solid, mp 80−81 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.92−7.88 (comp, 2H), 7.78 (s, 1H), 7.67−7.61 (comp, 3H), 7.60−7.55 (comp, 2H), 7.52 (dd, $J$ = 11.1, 3.7 Hz, 1H), 7.48−7.42 (comp, 3H), 7.38 (dd, $J$ = 15.9, 7.7 Hz, 3H), 6.88−6.83 (m, 1H), 2.79−2.72 (comp, 2H), 2.58−2.51 (comp, 2H), 1.98−1.90 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.8, 189.5, 143.2, 141.7, 140.0, 134.6, 134.2, 133.8, 133.1, 132.0, 131.0, 128.9, 128.6, 128.2, 127.7, 127.1, 126.9, 81.6, 34.1, 32.7, 22.2. IR (neat) 3342, 2953, 1728, 1674, 1487, 1229, 1008, 735, 696 cm$^{-1}$; HRMS (EI) *m*/*z* calculated for $C_{27}H_{21}N_2O_2$ [M − H]$^-$ 405.1609, found: 405.1604.

*5-Benzoyl-3-(4-bromophenyl)-5-(cyclopent-1-en-1-yl)-1,5-dihydro-4H-pyrazol-4-one (**10e**).* 60.4 mg, 74% yield. Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.19−8.14 (comp, 2H), 7.97−7.92 (comp, 3H), 7.61−7.57 (m, 1H), 7.52−7.49 (comp, 2H), 7.47−7.43 (comp, 2H), 5.86−5.83 (m, 1H), 2.47−2.39 (comp, 3H), 2.32−2.26 (m, 1H), 1.96−1.89 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 191.7, 189.5, 142.7, 138.3, 134.1, 133.3, 131.8, 131.7, 130.8, 128.4, 128.1, 127.4, 123.4, 81.7, 32.5, 32.4, 22.9. IR (neat) 3336, 1724, 1673, 1231, 1009 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{17}N_2O_2NaBr$ [M + Na]$^+$ 431.0366, found: 431.0350.

*5-Benzoyl-5-(4-bromophenyl)-3-(cyclopent-1-en-1-yl)-1,5-dihydro-4H-pyrazol-4-one (**11e**).* 10.6 mg, 13% yield. Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.83−7.79 (comp, 2H), 7.62 (s, 1H), 7.54−7.50 (comp, 3H), 7.39−7.35 (comp, 2H), 7.26−7.23 (comp, 2H), 6.83−6.80 (m, 1H), 2.74−2.68 (comp, 2H), 2.54−2.50 (comp, 2H), 1.95−1.89 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.4, 189.1, 143.3, 134.7, 134.6, 133.9, 132.9, 132.6, 131.9, 130.8, 128.7, 128.2, 123.2, 81.0, 77.3, 77.0, 76.8, 34.1, 32.7, 22.2. IR (neat) 3338, 1719, 1674, 1230, 908 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{17}N_2O_2NaBr$ [M + Na]$^+$ 431.0366, found: 431.0345.

*5-Benzoyl-3-(4-chlorophenyl)-5-(cyclopent-1-en-1-yl)-1,5-dihydro-4H-pyrazol-4-one (**10f**).* 50.2 mg, 69% yield. Yellow solid, mp 77.5−78.5 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.17 (d, $J$ = 8.5 Hz, 2H), 8.02 (d, $J$ = 8.5 Hz, 2H), 7.91 (s, 1H), 7.62−7.57 (m, 1H), 7.49−7.45 (comp, 2H), 7.38−7.34 (comp, 2H), 5.87−5.83 (m, 1H), 2.49−2.39 (comp, 3H), 2.33−2.26 (m, 1H), 1.97−1.88 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 191.8, 189.5, 142.7, 138.3, 135.0, 134.1, 133.3, 131.8, 130.7, 128.7, 128.4, 127.6, 127.2, 81.7, 32.5, 32.4, 22.9. IR (neat) 3345, 1716, 1673, 1231, 1116 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{17}N_2O_2NaCl$ [M + Na]$^+$ 387.0871, found: 387.0857.

*5-Benzoyl-5-(4-chlorophenyl)-3-(cyclopent-1-en-1-yl)-1,5-dihydro-4H-pyrazol-4-one (**11f**).* 10.2 mg, 14% yield. Yellow solid, mp 94−95 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.84−7.80 (comp, 2H), 7.67 (s, 1H), 7.55−7.51 (m, 1H), 7.40−7.36 (comp, 4H), 7.34−7.30 (comp, 2H), 6.85−6.81 (m, 1H), 2.75−2.69 (comp, 2H), 2.56−2.51 (copm, 2H), 1.96−1.90 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.5, 189.1, 143.3, 135.0, 134.5, 134.1, 133.9, 132.9, 131.9, 130.8, 129.7, 128.6, 127.9, 80.9, 34.1, 32.7, 22.2. IR (neat) 3344, 1717, 1671, 1228, 933 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{21}H_{17}N_2O_2NaCl$ [M + Na]$^+$ 387.0871, found: 387.0858.

*5-Benzoyl-5-(cyclopent-1-en-1-yl)-3-[4-(trifluoromethyl)phenyl]-1,5-dihydro-4H-pyrazol-4-one (**10g**).* 40.6 mg, 51% yield. Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.22−8.16 (comp, 4H), 8.07 (br, 1H), 7.63 (d, $J$ = 8.5 Hz, 2H), 7.60−7.56 (m, 1H), 7.50−7.47 (comp, 2H), 5.88−5.86 (m, 1H), 2.47−2.40 (comp, 3H), 2.33−2.27 (m, 1H), 1.98−1.89 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 191.4, 189.3, 141.9, 138.1, 134.2, 133.6, 133.3, 132.8, 132.6, 131.9(q, $J$ = 30.0 Hz), 129.3, 128.4, 127.9, 125.4 (q, $J$ = 3.8 Hz) 124.5 (q, $J$ = 278.8 Hz), 81.9, 32.4, 32.4, 23.0. IR (neat) 3334, 1709, 1673, 1321, 1120 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{22}H_{17}N_2O_2F_3Na$ [M + Na]$^+$ 421.1134, found: 421.1116.

*5-Benzoyl-3-(cyclopent-1-en-1-yl)-5-[4-(trifluoromethyl)phenyl]-1,5-dihydro-4H-pyrazol-4-one (**11g**).* 17.5 mg, 22% yield. Yellow solid, mp 45.5−46.5 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.82−7.76 (comp, 2H), 7.68−7.63 (comp, 3H), 7.55−7.50 (comp, 3H), 7.38 (t, $J$ = 7.8 Hz, 2H), 6.85−6.83 (m, 1H), 2.75−2.69 (comp, 2H), 2.56−2.51 (comp, 2H), 1.97−1.89 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.1, 188.9, 143.3, 139.3, 134.8, 134.1, 132.9, 131.8, 131.0 (q, $J$ = 32.5 Hz) 130.6 128.8, 126.9, 126.4 (q, $J$ = 3.8 Hz), 121.5 (q, $J$ = 270 Hz) 80.8, 34.1, 32.7, 22.2. IR (neat) 3335, 1729, 1675, 1119, 907 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{22}H_{17}N_2O_2F_3Na$ [M + Na]$^+$ 421.1134, found: 421.1119.

*5-Benzoyl-5-(cyclopent-1-en-1-yl)-3-(thiophen-2-yl)-1,5-dihydro-4H-pyrazol-4-one (**10h**).* 39.7 mg, 59% yield.[20] Yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.18 (d, $J$ = 7.3 Hz, 2H), 7.82 (s, 1H), 7.80 (dd, $J$ = 3.7, 0.8 Hz, 1H), 7.60 (t, $J$ = 7.4 Hz, 1H), 7.47 (t, $J$ = 7.8 Hz, 2H), 7.35 (d, $J$ = 5.1 Hz, 1H), 7.08 (dd, $J$ = 4.9, 3.8 Hz, 1H), 5.88−5.84 (m, 1H), 2.48−2.37 (comp, 3H), 2.37−2.26 (m, 1H), 1.91 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 190.7, 189.5, 141.6, 138.3, 134.1, 130.7, 128.4, 127.7, 126.7, 81.2, 32.4, 23.0. IR (neat) 3337, 2926, 1722, 1674, 1228, 731, 692 cm$^{-1}$; HRMS (ESI) $m/z$ calculated for $C_{19}H_{16}N_2O_2SNa$ [M + Na]$^+$ 359.0825, found: 359.0823.

*5-Benzoyl-5-(cyclohex-1-en-1-yl)-3-phenyl-1,5-dihydro-4H-pyrazol-4-one (**10i**).* 39.2 mg, 57% yield. Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J$ = 5.3, 3.3 Hz, 2H), 8.13−7.95 (m, 2H), 7.84 (s, 1H), 7.59 (ddd, $J$ = 6.7, 4.0, 1.3 Hz, 1H), 7.52−7.43 (comp, 2H), 7.42−7.32 (comp, 3H), 5.84 (t, $J$ = 2.7 Hz, 1H), 2.11 (comp, 2H), 1.63 (comp, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.3, 190.4, 143.7, 134.1, 133.9, 133.5, 130.8, 129.2, 129.1, 128.5, 128.5, 128.3, 128.2, 127.7, 126.0, 84.9, 25.9, 25.5, 22.6, 21.6. IR (neat) 3343, 2927, 1729, 1674, 1447, 1231, 695 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{22}H_{19}N_2O_2$ [M − H]$^-$ 343.1452, found: 343.1449.

*5-Benzoyl-3-(cyclohex-1-en-1-yl)-5-phenyl-1,5-dihydro-4H-pyrazol-4-one (**11i**).* 11.0 mg, 16% yield. Yellow solid, mp 63−64 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.83 (dd, $J$ = 8.4, 1.2 Hz, 2H), 7.56 (br, 1H), 7.49 (dd, $J$ = 10.5, 4.4 Hz, 1H), 7.41−7.31 (comp, 7H), 7.02 (m, 1H), 2.40 (comp, 2H), 2.18 (comp, 2H), 1.76−1.55 (comp, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.1, 189.6, 145.0, 135.9, 133.7, 133.1, 131.5, 131.0, 129.5, 128.7, 128.5, 127.7, 126.5, 82.1, 25.7, 25.2, 22.3, 21.9. IR (neat) 3339, 2927, 1732, 1675, 1447, 1231, 698 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{22}H_{19}N_2O_2$ [M − H]$^-$ 343.1452, found: 343.1448.

*5-Benzoyl-5-(cyclododec-1-en-1-yl)-3-phenyl-1,5-dihydro-4H-pyrazol-4-one (**10j**).* 43.7 mg, 51% yield. Yellow solid, mp 69−70 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.15−8.05 (comp, 2H), 7.89 (s, 1H), 7.64−7.31 (comp, 8H), 5.48−5.42 (m, 1H), 2.69−2.44 (comp, 2H), 2.32−2.18 (m, 1H), 2.09−1.96 (m, 1H), 1.55−1.19 (comp, 16H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.2, 190.3, 143.5, 143.5, 135.7, 135.0, 133.7, 131.6, 131.4, 129.0, 128.5, 128.2, 127.8, 127.1, 125.9, 85.7, 26.4, 25.53, 25.48, 25.09, 25.05, 24.74, 24.72, 24.1, 22.6, 22.4. IR (neat) 3351, 2928, 1699, 1677, 1448, 1344, 693 cm$^{-1}$; HRMS (ESI) $m/z$ calculated for $C_{28}H_{32}N_2O_2Na$ [M + Na]$^+$ 451.2356, found: 451.2347.

*5-Benzoyl-3-(cyclododec-1-en-1-yl)-5-phenyl-1,5-dihydro-4H-pyrazol-4-one (**11j**).* 30.0 mg, 35% yield. Yellow solid, mp 71−72 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 (dt, $J$ = 8.5, 1.5 Hz, 2H), 7.66 (s, 1H), 7.52−7.47 (m, 1H), 7.44−7.31 (comp, 7H), 6.79 (t, $J$ = 8.1 Hz, 1H), 2.57 (t, $J$ = 6.8 Hz, 2H), 2.30−2.17 (comp, 2H), 1.67−1.59 (comp, 2H), 1.54 (dt, $J$ = 9.6, 7.2 Hz, 2H), 1.49−1.41 (comp, 4H), 1.40−1.31 (comp, 6H), 1.30−1.23 (comp, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.4, 189.6, 145.0, 136.0, 135.4, 133.6, 133.2, 130.9, 129.9, 129.5, 128.7, 128.5, 126.5, 81.9, 26.6, 26.1, 25.6, 25.2, 25.1, 24.9, 24.6, 23.7, 22.9, 22.2. IR (neat) 3347, 2924, 2850, 1729, 1672, 1447, 1229, 737, 696 cm$^{-1}$; HRMS (ESI) $m/z$ calculated for $C_{28}H_{32}N_2O_2Na$ [M + Na]$^+$ 451.2356, found: 451.2349.

*5-Benzoyl-5-(3,6-dihydro-2H-pyran-4-yl)-3-phenyl-1,5-dihydro-4H-pyrazol-4-one (**10k**).* 24.9 mg, 36% yield. Yellow solid, mp 67−68 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.23−8.12 (comp, 2H), 8.10−8.03 (m, 1H), 7.84 (dd, $J$ = 6.3, 3.1 Hz, 1H), 7.56−7.30 (comp, 5H), 7.27 (comp, 2H), 5.91−5.88 (m, 1H), 4.22 (dd, $J$ = 5.3, 2.6 Hz, 2H), 3.89 (ddt, $J$ = 16.8, 11.9, 6.2 Hz, 1H), 3.78−3.64 (m, 1H), 2.70−2.41 (m, 1H), 2.37−2.05 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 191.8, 189.6, 144.1, 134.2, 131.7, 131.6, 131.0, 130.7, 129.4, 128.6, 128.5, 126.7, 126.0, 83.5, 65.3, 64.0, 25.8. IR (neat) 3332, 2925, 2085, 1710, 1677, 1447, 1232, 700 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{21}H_{17}N_2O_3$ [M − H]$^-$ 345.1245, found: 345.1243.

*5-Benzoyl-3-(3,6-dihydro-2H-pyran-4-yl)-5-phenyl-1,5-dihydro-4H-pyrazol-4-one (**11k**).* 6.9 mg, 10% yield. Yellow solid, mp 70−71 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J$ = 8.3 Hz, 2H), 7.73 (s, 1H), 7.52 (td, $J$ = 7.6, 1.0 Hz, 1H), 7.44−7.33 (comp, 7H), 6.99 (m, 1H), 4.29 (comp, 2H), 3.89 (dd, $J$ = 10.5, 5.2 Hz, 2H), 2.54 (comp, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.6, 189.3, 143.2, 135.6, 133.8, 133.0, 130.9, 129.6, 128.9, 128.5, 128.5, 126.4, 125.1, 82.4, 65.4, 64.1, 25.1. IR (neat) 3322, 2923, 2085, 1708, 1675, 1447, 1232, 1131, 694 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{21}H_{17}N_2O_3$ [M − H]$^-$ 345.1245, found: 345.1239.

*5-(4-Chlorobenzoyl)-5-(cyclopent-1-en-1-yl)-3-phenyl-1,5-dihydro-4H-pyrazol-4-one (**10l**).* 45.1 mg, 62% yield. Yellow solid, mp 85−86 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.21−8.15 (comp, 2H), 8.08−8.03 (comp, 2H), 7.92 (s, 1H), 7.46−7.43 (comp, 2H), 7.41−7.37 (comp, 3H), 5.85−5.82 (m, 1H), 2.47−2.40 (comp, 3H), 2.29−2.24 (m, 1H), 1.97−1.88 (comp, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.0, 188.7, 143.9, 140.7, 138.4, 132.4, 132.1, 131.5, 129.3, 129.0, 128.7, 128.5, 126.0, 81.6, 77.3, 77.0, 76.8, 32.5, 32.4, 22.9. IR (neat) 3347, 1724, 1674, 1114, 1010 cm$^{-1}$; HRMS (ESI) $m/z$ calculated for $C_{21}H_{17}N_2O_2NaCl$ [M + Na]$^+$ 387.0871, found: 387.0855.

*5-(4-Chlorobenzoyl)-3-(cyclopent-1-en-1-yl)-5-phenyl-1,5-dihydro-4H-pyrazol-4-one (**11l**).* 13.1 mg, 18% yield. Yellow solid, mp 92−93 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.84−7.80 (comp, 2H), 7.77 (s, 1H), 7.40−7.36 (comp, 3H), 7.33−7.30 (comp, 2H), 7.28−7.26 (comp, 2H), 6.82−6.79 (m, 1H), 2.75−2.71 (comp, 2H), 2.55−2.51 (comp, 2H), 1.95−1.89 (comp, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.7, 188.4, 143.3, 140.5, 135.7, 134.1, 132.7, 132.0, 131.0, 129.6, 129.0, 128.8, 126.7, 82.2, 77.3, 77.0, 76.8, 34.1, 32.7, 22.2. IR (neat) 3342, 1741, 1676, 1091, 907 cm$^{-1}$; HRMS (ESI) $m/z$ calculated for $C_{21}H_{17}N_2O_2NaCl$ [M + Na]$^+$ 387.0871, found: 387.0856.

*5-(Cyclopent-1-en-1-yl)-5-(4-methoxybenzoyl)-3-phenyl-1,5-dihydro-4H-pyrazol-4-one (**10m**).* 34.6 mg, 48% yield. Yellow solid, mp 53−54 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.29−8.18 (comp, 2H), 8.11−8.02 (comp, 2H), 7.98 (s, 1H), 7.43−7.33 (comp, 3H), 6.98−6.90 (comp, 2H), 5.88−5.79 (m, 1H), 3.89 (s, 3H), 2.52−2.37 (comp, 3H), 2.32−2.24 (m, 1H), 2.00−1.84 (comp, 2H). $^{13}$C NMR (126 MHz, cdcl$_3$) $\delta$ 192.6, 187.8, 164.2, 144.0, 139.0, 133.6, 131.4, 129.2, 129.1, 128.5, 126.1, 126.0, 113.6, 81.6, 55.5, 32.6, 32.4, 23.0. IR (neat) 3336, 2932, 2842, 1714, 1663, 1596, 1244, 1171, 1028, 842, 732 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{22}H_{19}N_2O_3$ [M − H]$^-$ 359.1401, found: 359.1397.

*3-(Cyclopent-1-en-1-yl)-5-(4-methoxybenzoyl)-5-phenyl-1,5-dihydro-4H-pyrazol-4-one (**11m**).* 20.9 mg, 29% yield. Yellow solid, mp 72−73 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.94−7.84 (comp, 2H), 7.78 (s, 1H), 7.41−7.34 (comp, 3H), 7.33−7.29 (comp, 2H), 6.86−6.77 (comp, 3H), 3.81 (s, 3H), 2.77−2.69 (comp, 2H), 2.53 (ddd, $J$ = 9.6, 4.8, 2.2 Hz, 2H), 1.93 (dt, $J$ = 15.0, 7.4 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.4, 187.8, 163.9, 143.4, 136.4, 133.9, 133.8, 132.1, 129.4, 128.9, 128.7, 126.7, 125.5, 113.7, 82.2, 55.5, 34.1, 32.7, 22.2. IR (neat) 3310, 2933, 2841, 1736, 1667, 1599, 1510, 1247, 1172, 733 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{22}H_{19}N_2O_3$ [M − H]$^-$ 359.1401, found: 359.1394.

*5-(Cyclopent-1-en-1-yl)-5-(4-methoxybenzoyl)-3-(4-methoxyphenyl)-1,5-dihydro-4H-pyrazol-4-one (**10n**).* 42.9 mg, 55% yield. Yellow solid, mp 52−53 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.29−8.17 (comp, 2H), 8.07−7.98 (comp, 2H), 7.90 (s, 1H), 6.97−6.87 (comp, 4H), 5.86−5.78 (m, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.51−2.36 (comp, 3H), 2.28 (dddd, $J$ = 15.3, 9.3, 5.8, 2.1 Hz, 1H), 1.99−1.84 (comp, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.0, 187.9, 164.2, 160.4, 144.2, 139.2, 133.5, 131.1, 127.6, 126.2, 121.8, 113.9, 113.6, 81.3, 55.5, 55.3, 32.5, 32.4, 23.0. IR (neat) 3340, 2956, 2840, 1717, 1665, 1598, 1508, 1248, 1172, 1029, 837 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{23}H_{21}N_2O_4$ [M − H]$^-$ 389.1507, found: 389.1501.

*3-(Cyclopent-1-en-1-yl)-5-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-1,5-dihydro-4H-pyrazol-4-one (**11n**).* 18.7 mg, 24% yield. Yellow solid, mp 67−68 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.94−7.86 (comp, 2H), 7.83 (s, 1H), 7.24−7.17 (comp, 2H), 6.92−6.85 (comp, 2H), 6.86−6.77 (comp, 3H), 3.81 (s, 3H), 3.80−3.77 (s, 3H), 2.77−2.67 (comp, 2H), 2.56−2.46 (comp, 2H), 1.96−1.87 (comp, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.7, 188.0, 163.8, 159.7, 143.3, 133.9, 133.6, 132.2, 128.5, 128.1, 125.6, 114.8, 113.6, 82.0, 55.5, 55.3, 34.1, 32.7, 22.2. IR (neat) 3337, 2933, 2839, 1721, 1663, 1596, 1508, 1241, 1169, 1027, 839, 734 cm$^{-1}$; HRMS (EI) $m/z$ calculated for $C_{23}H_{21}N_2O_4$ [M − H]$^-$ 389.1507, found: 389.1497.

*5-(Cyclopent-1-en-1-yl)-5-(4-methoxybenzoyl)-3-[4-(trifluoromethyl)phenyl]-1,5-dihydro-4H-pyrazol-4-one (**10o**).* 36.0 mg, 42% yield. Yellow solid, mp 35−36 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.23 (comp, 5H), 7.63 (d, $J$ = 8.3 Hz, 2H), 6.99−6.91 (comp, 2H), 5.89−5.83 (m, 1H), 3.89 (s, 3H), 2.51−2.39 (comp, 3H), 2.33−2.24 (m, 1H), 2.00−1.87 (comp, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 191.9, 187.4, 164.4, 141.9, 138.6, 133.6, 131.7, 130.5 (q, $J$ = 32.8 Hz), 125.9, 125.4 (q, $J$ = 3.8 Hz), 113.6, 82.0, 55.5, 32.5, 32.4, 23.0. IR (neat) 3326, 2930, 2845, 1663, 1596, 1321, 1243, 1164, 1065, 842 cm$^{-1}$;

HRMS (EI) *m*/*z* calculated for $C_{23}H_{18}F_3N_2O_3$ [M − H]$^-$ 427.1275, found: 427.1274.

*3-(Cyclopent-1-en-1-yl)-5-(4-methoxybenzoyl)-5-[4-(trifluoromethyl)phenyl]-1,5-dihydro-4H-pyrazol-4-one (**11o**).* 4.3 mg, 5% yield. Yellow solid, mp 67−68 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.85 (dd, *J* = 9.3, 2.6 Hz, 2H), 7.71 (s, 1H), 7.66 (dd, *J* = 8.5, 2.5 Hz, 2H), 7.48 (dd, *J* = 8.5, 2.5 Hz, 2H), 6.92−6.76 (comp, 3H), 3.84 (s, 3H), 2.82−2.67 (comp, 2H), 2.61−2.42 (comp, 2H), 2.00−1.84 (comp, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.8, 187.1, 164.2, 143.6, 140.1, 134.6, 133.6, 131.9, 130.8 (q, *J* = 34.0 Hz), 127.7, 127.1, 126.3 (q, *J* = 3.8 Hz), 125.2, 125.1, 114.0, 81.2, 55.6, 34.1, 32.7, 22.2. IR (neat) 3337, 2930, 1725, 1667, 1598, 1323, 1243, 1170, 1120, 1070, 841 cm$^{-1}$; HRMS (EI) *m*/*z* calculated for $C_{23}H_{18}F_3N_2O_3$ [M − H]$^-$ 427.1275, found: 427.1277.

*5-Benzoyl-3-phenyl-5-(prop-1-en-2-yl)-1,5-dihydro-4H-pyrazol-4-one (**10p**).* 36.5 mg, 60% yield.[20] Yellow solid, mp 39−40 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.19 (d, *J* = 7.4 Hz, 2H), 8.08 (d, *J* = 6.7 Hz, 2H), 7.93 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43−7.35 (comp, 3H), 5.27 (s, 1H), 5.20 (s, 1H), 1.91 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.0, 189.9, 143.7, 140.3, 134.1, 133.4, 130.7, 129.3, 129.0, 128.5, 128.5, 126.0, 116.7, 84.1, 20.0. IR (neat) 3339, 1727, 1671, 1447, 1229, 692 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{19}H_{16}N_2O_2Na$ [M + Na]$^+$ 327.1104, found: 327.1098.

*5-Benzoyl-3-(4-methoxyphenyl)-5-(prop-1-en-2-yl)-1,5-dihydro-4H-pyrazol-4-one (**10q**).* 48.1 mg, 72% yield.[20] Yellow solid, mp 44−45 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.18 (d, *J* = 7.4 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.74 (s, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.25 (s, 1H), 5.18 (s, 1H), 3.83 (s, 3H), 1.90 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 192.4, 190.0, 160.5, 144.1, 140.5, 134.1, 133.4, 130.7, 128.4, 127.6, 121.6, 116.5, 114.0, 83.9, 55.3, 20.0. IR (neat) 3342, 2934, 1730, 1674, 1251, 1231, 1173, 835, 690 cm$^{-1}$; HRMS (EI) *m*/*z* calculated for $C_{20}H_{17}N_2O_3$ [M − H]$^-$ 333.1245, found: 333.1251.

**Synthesis of 4-Hydroxypyrazoles.** The experiments were carried out with both: (*a*) reaction mixtures containing **10d** + **11d** and (*b*) individual compounds **10d** or **11d**.

*Procedure for the Synthesis of **6d** from a Reaction Mixture Containing **10d** and **11d**.* To the reaction mixture after the gold(I)-catalyzed reaction of **9d** that contained 1,5-dihydro-4*H*-pyrazol-4-ones **10d** and **11d** (156 mg, 0.384 mmol) in DCE (8.0 mL) was added benzylamine (49.4 mg, 0.461 mmol) dissolved in DCE (0.5 mL) in one portion under a nitrogen atmosphere. The resulting mixture was stirred at 20 °C for 2 h, and the white precipitate of **6′** was formed. The precipitate of **6′** was dissolved by adding methanol (5.0 mL); the solution was filtered through Celite to remove gold particles. Solvents were evaporated, and the obtained mixture of products **6′** and *N*-benzylbenzamide was separated by column chromatography using hexanes/ethyl acetate (v/v 2:1) as the eluent to afford *3-([1,1′-biphenyl]-4-yl)-5-(cyclopent-1-en-1-yl)-1H-pyrazol-4-ol* (**6′**) (100 mg, 87% yield) as a white solid; mp > 300 °C (decomp.). $^1$H NMR (300 MHz, DMSO-d6) $\delta$ 12.54 (br, 1H), 8.04−8.01 (comp, 3H), 7.69 (d, *J* = 7.3 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 6.29 (s, 1H), 2.70−2.68 (comp, 2H), 2.49−2.47 (comp, 2H), 1.99−1.78 (comp, 2H). $^{13}$C NMR (126 MHz, DMSO-d6) $\delta$ 140.3, 138.7, 136.0, 129.4, 127.8, 127.1, 126.9, 126.3, 126.0, 33.4, 33.3, 22.8. IR (neat) 3246 (br), 1634, 1487, 1269, 1016, 844, 767 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{20}H_{19}N_2O$ [M + H]$^+$ 303.1492, found: 303.1496.

*5-(Cyclopent-1-en-1-yl)-3-phenyl-1H-pyrazol-4-ol (**6**).* 81.3 mg, 90% yield. White solid, mp 198−200 °C (decomp.). $^1$H NMR (500 MHz, $CD_3OD$) $\delta$ 7.85 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.45−7.42 (m, 2H), 7.35−7.32 (m, 1H), 6.48 (dt, *J* = 4.2, 2.1 Hz, 1H), 2.78 (ddd, *J* = 9.8, 4.4, 2.1 Hz, 2H), 2.57 (tdd, *J* = 7.5, 4.8, 2.4 Hz, 2H), 2.07−1.93 (comp, 2H). $^{13}$C NMR (126 MHz, $CD_3OD$) $\delta$ 136.7, 135.1, 134.3, 131.6, 130.4, 128.7, 128.2, 127.5, 126.1, 32.9, 32.6, 22.4. IR (neat) 3249 (br), 1635, 1482, 1274, 1026, 845 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{14}H_{15}N_2O$ [M + H]$^+$ 227.1179, found: 227.1181.

*Procedure for the Synthesis of **6′** from Pure **10d**.* To a solution of **10d** (81.0 mg, 0.200 mmol) in DCE (4.0 mL) was added benzylamine (25.7 mg, 0.240 mmol) dissolved in DCE (0.3 mL) in one portion under a nitrogen atmosphere. The resulting mixture was stirred at 20 °C for 2 h. Afterward, DCE was evaporated, and the obtained mixture of products **6′** and *N*-benzylbenzamide was separated by column chromatography using hexanes/ethyl acetate (v/v 2:1) as the eluent to afford compound **6′** (54.0 mg, 89% yield). The same procedure was used for the synthesis of **6′** from **11d**.

**Gold-Catalyzed Reactions of Propargyl Diazoacetates 14−16.** *General Procedure for the Catalysis by AuCl($C_4H_8S$).* To a stirred solution of propargyl diazoacetate (0.30 mmol) in DCE (2.0 mL) was rapidly added AuCl($C_4H_8S$) (4.8 mg, 0.015 mmol) dissolved in DCE (1.0 mL) under a nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 12 h (**16**) or at 84 °C for 48 h (**14** and **15**). Solvent was evaporated, and the reaction mixture was purified via flash chromatography (using gradient hexanes to 9:1 hexanes/ethyl acetate as the eluent) to afford compounds **17** and **18**. Reported in Scheme 8 are isolated yields.

*3-Methyl-1-phenylbut-2-en-1-one (**17**).*[21] Pale yellow liquid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.93 (d, *J* = 8.1 Hz, 2H), 7.58−7.37 (comp, 3H), 6.75 (s, 1H), 2.21 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 191.5, 156.6, 139.2, 132.3, 128.4, 128.2, 121.2, 28.0, 21.2.

*(3-Methylbut-3-en-1-yn-1-yl)benzene (**18**).*[22] Colorless liquid. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.52−7.42 (comp, 2H), 7.39−7.29 (comp, 3H), 5.43 (s, 1H), 5.33 (s, 1H), 2.02 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 131.7, 131.6, 128.3, 126.9, 123.3, 122.0, 90.6, 88.5, 23.5.

*General Procedure for the Catalysis by $AuPicCl_2$.* To a stirred solution of propargyl diazoacetate **14** (81 mg, 0.30 mmol) in DCE (2.0 mL) was rapidly added $AuPicCl_2$ (5.9 mg, 0.015 mmol) dissolved in DCE (1.0 mL) under a nitrogen atmosphere, and the reaction mixture was stirred at 40 °C for 12 h. Solvent was evaporated, and the reaction mixture was purified via flash chromatography (using gradient 19:1 hexanes/ethyl acetate to 9:1 hexanes/ethyl acetate as the eluent) to afford **17** (6.7 mg, 14%) and **21** (66.4 mg, 82%).

*(Z)-3-Methyl-1-phenylbuta-1,3-dien-1-yl 2-Diazo-3-oxobutanoate (**21**).* Yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.49−7.40 (comp, 2H), 7.35−7.27 (comp, 3H), 2.49 (s, 3H), 1.83 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 190.3, 159.6, 131.8, 128.6, 128.2, 122.2, 89.2, 85.0, 74.7, 29.4, 28.3. IR (neat) 2925, 2142, 1726, 1659, 1246, 1139, 1058, 697 cm$^{-1}$; HRMS (ESI) *m*/*z* calculated for $C_{15}H_{14}N_2O_3Na$ [M + Na]$^+$ 293.0897, found: 293.0888.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01833.

Experimental tables, kinetic experiments details, copies of $^1$H and $^{13}$C NMR spectra of all compounds, and crystallographic reports (PDF)

Crystallographic data for **4** (CIF)

Crystallographic data for **6′** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Support for this research from the National Science Foundation (CHE-1533833 and CHE-1464690), The Welch Foundation (AX-1871), and UTSA is gratefully acknowledged. H.Q. thanks the China Scholarship Council for a fellowship. The HRMS used in this research is supported by a grant from the National Institutes of Health (G12MD007591). We thank W. G. Griffith for extensive mass spectral analyses.

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DOI: 10.1021/acs.joc.6b01833
J. Org. Chem. 2016, 81, 9235−9246